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EFFECTS OF EXPANSION OF THE Π-ELECTRON SYSTEM ON PHOTOCURRENT QUANTUM YIELDS FOR PORPHYRIN PHOTOCELLS: MAGNESIUM AND ZINC TETRABENZPORPHYRIN SENSITIZERS

Kazuo YAMASHITA
Department of Environment Science, Faculty of Integrated Arts and Sciences, Hiroshima University, Hiroshima 730

Expansion of the porphyrin π-system by peripheral substitution lowers the oxidation potential of the macrocycle and increases the photocurrent quantum yield obtained when the porphyrin is used as sensitizer in a photocell. Tetrabenzporphyrins fall among the most efficient porphyrin sensitizers studied so far with photocurrent quantum yields greater than 10% in the Al/Porphyrin/0.1 mol dm^{-3} $K_3[Fe(CN)_6]$ and 0.1 mol dm^{-3} $K_4[Fe(CN)_6]$/Pt cell.

The photovoltaic and photoelectrochemical properties of chlorophylls,$^{1-4)}$ phthalocyanines,$^{5-7)}$ and porphyrins$^{8-12)}$ have been extensively studied as models of the photosynthetic apparatus and as potential sensitizers for conversion of solar energy into electric and/or chemical energy.

We previously found a correlation between the first ring oxidation potential and the photocurrent quantum yield of porphyrins, in which the more easily oxidized macrocycles exhibited the higher quantum yields.$^{9)}$ We also noted that peripheral substitution could modulate the oxidation potential, and that long aliphatic chain substituents decreased the quantum yields, presumably by acting as insulators towards electron transport. These results suggest that expansion of the porphyrin π-system may lead to lower oxidation potentials as well as facilitate energy and electron transfer by increasing π-π interactions between neighboring molecules, and result in an increase of photocurrents and the quantum yields.

We present here evidence that magnesium and zinc tetrabenzporphines (MgTBP and ZnTBP) are indeed oxidized very easily in comparison with other porphyrins and act as efficient sensitizers in simple photovoltaic or photoelectrochemical devices.

MgTBP and ZnTBP were kindly supplied by Profs. M. Gouterman and C.K. Chang and were purified by chromatography (Woelm alumina) followed by recrystallization 3 times from pyridine-methanol. The metals used as electrodes are silver, aluminium and platinum, of which the purity was better than 99.99%. Reagent grade dichloromethane was dried over activated 4A molecular sieves before distillation. Tetrabutylammonium perchlorate (TBAP) was recrystallized 3 times from ethylacetate-hexane. Two types of photocells were used: Al/Porphyrin/Ag and Al/Porphyrin/0.1 mol dm^{-3} $K_3[Fe(CN)_6]$ and 0.1 mol dm^{-3} $K_4[Fe(CN)_6]$/Pt. The semi-transparent film of aluminium was deposited onto a Corning 7059 glass slide at 10^{-4} Pa. The transmittance of the aluminium was 20-50%. The porphyrins were sublimed and deposited on the aluminium; no good films of MgTBP and ZnTBP were prepared by rapid evaporation of solutions using a photoresist spinner. The sandwich cells were completed

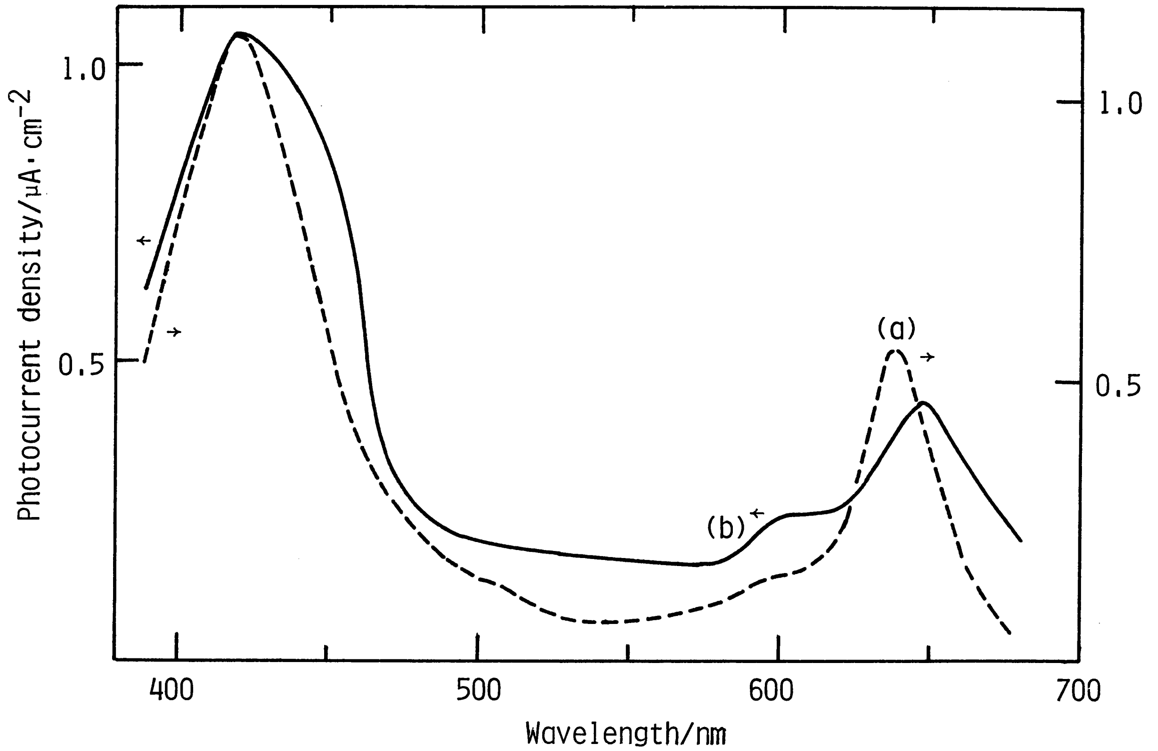

Fig. 1. Optical absorption and action spectra. (a)The absorption spectrum of the sublimed film of MgTBP and (b) the action spectrum of the photocurrent for the Al/MgTBP/Ag cell.

by vapor deposition of the silver electrode. The electrolyte cells were prepared using Pt wire immersed in a solution 0.1 mol dm^{-3} in $K_3[Fe(CN)_6]$ and 0.1 mol dm^{-3} in $K_4[Fe(CN)_6]$. Film thickness (∿0.01 μm for Al and ∿0.1 μm for the porphyrins) were measured with a Kronos QM-331 digital monitor. Voltages and currents generated by the photocells were monitored by a Keithley 602 electrometer. Optical absorption spectra were recorded on a Cary 17 or 219 spectrometer. Cyclic voltammograms were obtianed as described previously.13)

Figure 1 displays the optical absorption spectrum of a sublimed film of MgTBP and the photocurrent action spectrum obtained on illumination of the Al electrode. The correspondence between the two spectra establishes that the Al-porphyrin interface is photoactive region, as was previously found in similar porphyrin-sensitized devices. Similar results are obtained for ZnTBP. We further note that the tetrabenz-derivatives absorb throughout the range of visible light and the light absorbing properties approach those found for chlorophylls in *vivo* (λ_{max}=680 and 700 nm for Photosystems II and I of green plants, respectively).

We have previously noted a correlation between the ease of oxidation of the porphyrins and higher quantum yields. Then we deduced that the rate constant of the charge carrier formation process correlates exponentially with the oxidation potential of the porphyrin molecule at the ground state or excited state. The current quantum yield is in direct proportion to the rate constant. Hence, the photocurrent quantum yield may correlate exponentially with the oxidation potential.11) The first ring oxidation potentials of 0.24 and 0.40 V *vs.* SCE found for MgTBP and ZnTBP rank these macrocycles as the easiest to oxidize among a large variety of Mg and Zn porphyrins [Table 1, see also Felton's review14)]. From this result it is anticipated that MgTBP and ZnTBP will be

Table 1. Half-wave potentials of the first ring oxidation reactions of the porphyrins

Compound	Half-wave potential *vs.* SCE/V	Reference
MgTBP	0.23[a]	
ZnTBP	0.40[b]	
	0.38[c]	(15)
	0.36[d]	(16)
MgTPP	0.61[a]	
	0.54[e]	(17)
MgP	0.68[a]	
	0.60	(18)
ZnTPP	0.78[a]	
	0.79[f]	(19)
	0.71[e]	(17)
ZnP	0.80[a]	
	0.72	(18)

[a] Oxidation at Pt in CH_2Cl_2 with 0.1 mol dm^{-3} tetrabutylammonium perchlorate (TBAP). [b] In CH_2Cl_2 containing 1% pyridine with 0.1 mol dm^{-3} TBAP. [c] In dimethylsulfoxide (DMSO) with 0.1 mol dm^{-3} TBAP. [d] In DMSO with 1 mol dm^{-3} $LiClO_4$. [e] In butyronitrile with 0.1 mol dm^{-3} $LiClO_4$. [f] In benzonitrile with 1 mol dm^{-3} TBAP.

Abbreviations used: OEP, octaethylporphine; P, porphine; TBP, tetrabenzporphine; TPP, tetraphenylporphine.

Table 2. Photocurrent quantum yields[a] of the porphyrins

Compound	Wavelength/nm	Quantum yield	Reference
Al/Porphyrin/0.1 mol dm^{-3} $K_3[Fe(CN)_6]$ and 0.1 mol dm^{-3} $K_4[Fe(CN)_6]$/Pt cell			
MgP	420	2.0×10^{-1}	(9)
MgTBP	447	1.5×10^{-1}	
ZnTBP	440	1.2×10^{-1}	
ZnP	420	9.1×10^{-2}	(9)
MgTPP	445	9.8×10^{-2}	(9)
ZnTPP	440	3.0×10^{-2}	
		6.1×10^{-3}	(9)
Al/Porphyrin/Ag cell			
MgTBP	445	8.5×10^{-2}	
ZnTBP	460	4.5×10^{-2}	
MgTPP	440	5.2×10^{-2}	
ZnTPP	440	3.2×10^{-2}	

[a] Quantum yield is defined as the number of the electrons produced per photon absorbed by the porphyrin film at low light intensities (about 0.1 mW dm^{-2}).

the most effective sensitizers among the porphyrins studied. In fact they are little less efficient than magnesium porphine (MgP) as shown in Table 2. For a given porphyrin ligand, the quantum yields of the photocurrents parallel the first oxidation potential of the porphyrin (Fig. 2, in which the line shown represents a least squares fit to the tetraphenylporphyrin data), but all porphyrins do not fall on the same curve. These may be attributed to a combination of various factors such as a) the ease of charge carrier formation, relating with the oxidation potential of the porphyrin, b) the packing of porphyrin molecules in solid films, and c) the extent of π-π overlap between the porphyrin rings, which facilitates energy and electron transfer.

Comparison of the photocurrent

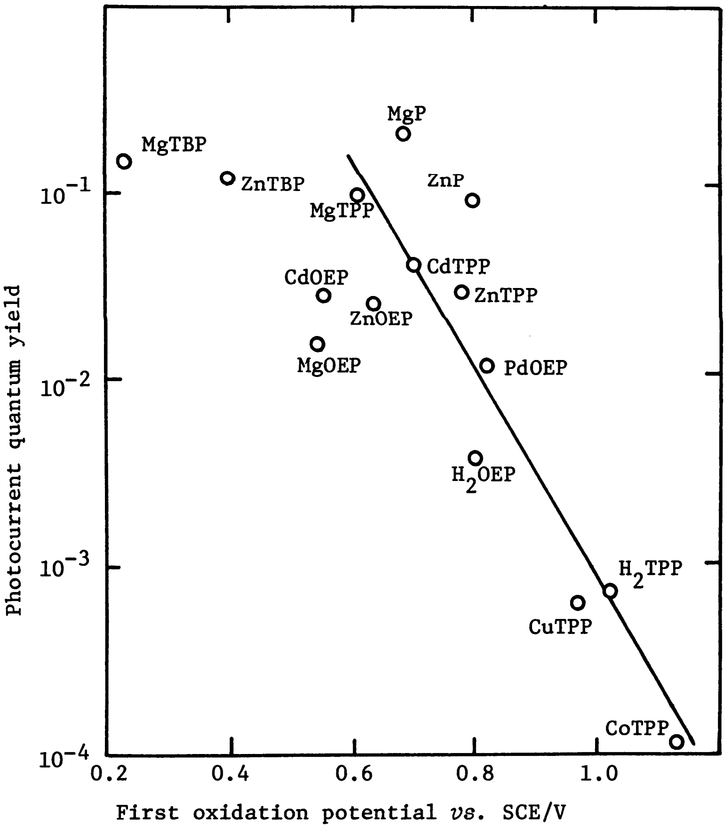

Fig. 2. Correlation between the quantum yields obtained for the Al/Porphyrin/0.1 mol dm^{-3} $K_3[Fe(CN)_6]$ and 0.1 mol dm^{-3} $K_4[Fe(CN)_6]$/Pt cells and the first ring oxidation potentials of the porphyrins in non-aqueous solvents. The oxidation potentials of TBP and TPP were measured using Pt electrode in CH_2Cl_2 with 0.1 mol dm^{-3} TBAP and those of OEP in butyronitrile with 0.1 mol dm^{-3} TBAP.[20)]

quantum yields found here with those obtained for other porphyrin derivatives shows distinctly that tetrabenz-compounds fall within the most efficient light converters investigated so far with the quantum yields greater than 10% in the electrolyte cell.

Thus the facile synthesis, chemical stability (ZnTBP can be heated in air without decomposing), light absorption properties and high quantum yields of tetrabenzporphyrins suggest that these macrocycles are attractive potential candidates for solar energy conversion devices.

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